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PECULIARITY IN THE FORMATION OF THE NITRILE-ESTERS OF DICARBOXY-GLUTACONIC ACID.

By Yoshiyuki URUSHIBARA.

Received November 14, 1929. Published January 28, 1930.

As the introduction to the present paper the previous studies on the synthesis of the nitrile-esters of dicarboxy-glutaconic acid[1] will be outlined. The condensation of the ethoxymethylene compound $XYC=CHOC_2H_5$ with the sodiomethylene compound $CHNaX'Y'$ can occur in nine different combinations if each of X, X', Y, and Y' represents either -CN or $-COOC_2H_5$; and the products of the nine cases should be different from one another, including all the possible nitrile-esters of dicarboxyglutaconic acid $(HOOC)_2C=CH-CH(COOH)_2$, if the condensation proceeds as follows:

$$\begin{matrix} X \\ Y \end{matrix}\!\!>\!C=CHOC_2H_5 + CHNa\!<\!\!\begin{matrix} X' \\ Y' \end{matrix} = \begin{matrix} X \\ Y \end{matrix}\!\!>\!C=CH-CNa\!<\!\!\begin{matrix} X' \\ Y' \end{matrix} + C_2H_5OH.$$

Nevertheless, if the nine condensations are carried out in alcoholic solutions, more than six compounds can not be obtained, for among the nine condensations three pairs yield respectively only one and the same product. In precise expression, the following pair of reactions does not yield two different products which can be expected by the equations:

$$XYC=CHOC_2H_5 + CHNaX'Y' = XYC=CH-CNaX'Y' + C_2H_5OH,$$
$$X'Y'C=CHOC_2H_5 + CHNaXY = X'Y'C=CH-CNaXY + C_2H_5OH.$$

The constitution of the only product has been determined. The sodium atom is always situated at the carbon atom to which the more carbethoxy-groups are attached. The six really obtained compounds are, therefore, as follows:

$(C_2H_5OCO)_2C=CH-CNa(COOC_2H_5)_2$, $C_2H_5OCO(CN)C=CH-CNa(COOC_2H_5)_2$,
$C_2H_5OCO(CN)C=CH-CNa(CN)COOC_2H_5$, $(CN)_2C=CH-CNa(COOC_2H_5)_2$,
$(CN)_2C=CH-CNa(CN)_2$, $(CN)_2C=CH-CNa(CN)COOC_2H_5$.

The following three can not be obtained:

$(C_2H_5OCO)_2C=CH-CNa(CN)COOC_2H_5$, $(C_2H_5OCO)_2C=CH-CNa(CN)_2$,
$C_2H_5OCO(CN)C=CH-CNa(CN)_2$.

Similarly, by the condensation of ethyl ethoxymethylene-cyanoacetate with methyl sodio-cyanoacetate in methyl alcohol and by the condensation

(1) This Bulletin, **2** (1927), 278; **3** (1928), 219.

of methyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate in ethyl alcohol, the same methyl ethyl sodio-dicyanoglutaconate and from it the same methyl ethyl dicyanoglutaconate semihydrate are obtained.

By and by, the author became aware of the studies on xanthophanic acids by Feist and his co-workers.[1] They describe γ-methyl α-ethyl α, γ-diacetyl-glutaconate and α-methyl γ-ethyl α, γ-diacetyl-glutaconate as different substances. They obtained the former by the condensation of methyl ethoxy-methylene-acetoacetate with ethyl sodio-acetoacetate in ether, and the latter by the condensation of ethyl ethoxy-methylene-acetoacetate with methyl sodio-acetoacetate.

The above two condensations carried out by the present author and giving the same methyl ethyl dicyanoglutaconate are not more different from those by Feist than that cyano-groups took the place of the acetyl-groups and methyl and ethyl alcohols were used as the solvents instead of ether. Thus, to make matters clear, it seemed important to try the synthesis of the nitrile-esters of dicarboxyglutaconic acid in the ethereal medium. For this purpose it is unnecessary to synthesize those compounds with equal attachments at the both ends of the propylene nucleus. The eight condensations shown later were tried; and if the results are collected it can be deduced that four kinds of products are possible in each reaction, and that in the condensation of $XYC=CHOC_2H_5$ with $CHNaX'Y'$, are possible the following four products:

$XYC=CH-CNaX'Y'$, the product of the 1st kind;
$X'Y'C=CH-CNaXY$, the product of the 2nd kind;
$X'Y'C=CH-CNaX'Y'$, the product of the 3rd kind;
$XYC=CH-CNaXY$, the product of the 4th kind.

If $X=X'$ and $Y=Y'$, the four formulae are the same; and in such cases, if the experiment were carried out, only one product would be obtained. The table shows the results of the eight condensations. Individual compounds found in each condensation are placed in the forms of the sodium derivatives under the general formulae showing the kinds. Compounds corresponding to the blank spaces could not be found. Unfortunately, in no reaction all of the possible products could be isolated. Probably, those formed in relatively large quantities or those easy of separation could be isolated. Besides, at the beginning of the experiments on this series of condensations it was beyond expectation that each reaction would give four kinds of products. It was after studying many of the reactions that possibility of four kinds of products was found.

(1) *Ber.*, **59** (1926), 2958.

The mechanism of the reactions can be explained to some extent, if they are compared with the experiments on the synthesis of poly-acetic acids of methane by C. K. Ingold and E. A. Perren.[1] According to them various derivatives of diethyl glutaconate readily react with ethyl sodiocyanoacetate; nevertheless the products of these condensations contain no trace of derivatives of methane triacetic acid, but consist almost wholly of fission products formed from these substances by a decomposition having the character of a retrograde Michael reaction. For instance, triethyl α-carboxyglutaconate gives initially a condensation product, which then undergoes complete fission into diethyl α-cyanoglutaconate and diethyl malonate:

$$C_2H_5OCOCH{=}CH{-}CH(COOC_2H_5)_2 + CNCH_2COOC_2H_5$$
$$\longrightarrow CH\begin{cases} CH(CN)COOC_2H_5 \\ CH_2COOC_2H_5 \\ CH(COOC_2H_5)_2 \end{cases}$$
$$\longrightarrow C_2H_5OCOCH{=}CH{-}CH(CN)COOC_2H_5 + CH_2(COOC_2H_5)_2.$$

In the second reaction the group eliminated from the molecule is usually the largest among the substituted acetic acid residues attached to the same carbon atom.

The mechanism of the reaction of the ethoxymethylene compound $XYC{=}CHOC_2H_5$ with the methylene compound $CH_2X'Y'$ which gives four products can be analysed into several processes. Previously[2] the formation of the intermediate addition compound $XYCH{-}CH(OC_2H_5){-}CHX'Y'$ was supposed, but such a hypothesis is not necessary, because the derivatives of methane triacetic acid act not only in place of it, but also in the formation of such products as not to be explained by the former hypothesis. The reaction begins with the formation of the product of the first kind:

$$XYC{=}CHOC_2H_5 + CH_2X'Y'$$
$$\longrightarrow XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind)} + C_2H_5OH.$$

The product of the first kind partly condenses with the methylene compound $CH_2X'Y'$ present in the reaction medium, and then fission follows:

$$XYC{=}CH{-}CHX'Y' + CH_2X'Y' \longrightarrow CH\begin{cases} CHXY \\ CHX'Y' \\ CHX'Y' \end{cases}$$
$$\longrightarrow \begin{cases} XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind)} + CH_2X'Y', \\ X'Y'C{=}CH{-}CHXY \text{ (the product of the 2nd kind)} + CH_2X'Y', \\ X'Y'C{=}CH{-}CHX'Y' \text{ (the product of the 3rd kind)} + CH_2XY. \end{cases}$$

(1) *J. Chem. Soc*, **119** (1921), 1582.
(2) This Bulletin, **3** (1928), 226.

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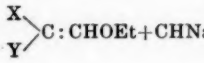
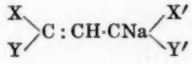
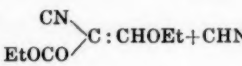
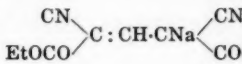
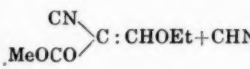
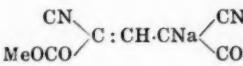
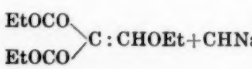
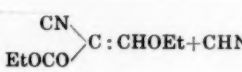
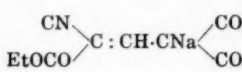
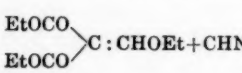
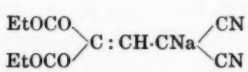
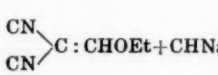
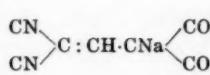
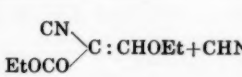
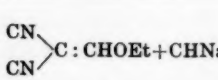
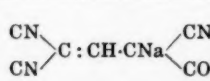
		
1		
2		
3		
4		
5		
6		
7		
8		

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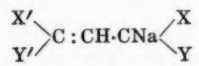	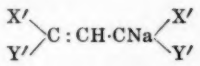	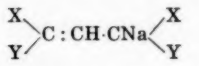
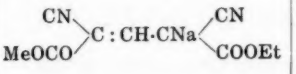		
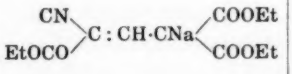	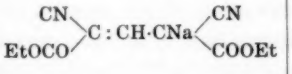	
	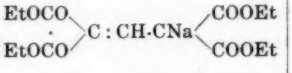	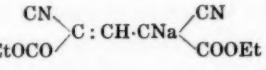
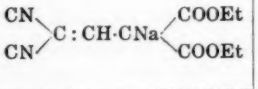		
	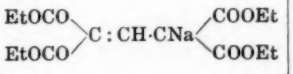	
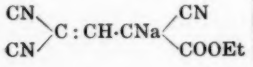		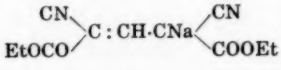

The fission is possible in three directions. Now, another methylene compound CH_2XY is ready to condense with the product of the first or the second kind, and fission can yield the fourth product besides others:

$$\left.\begin{matrix} XYC{=}CH{-}CHX'Y' + CH_2XY \\ X'Y'C{=}CH{-}CHXY + CH_2XY \end{matrix}\right\} \longrightarrow CH\begin{matrix} \swarrow CHXY \\ -CHXY \\ \searrow CHX'Y' \end{matrix}$$

$$\longrightarrow \begin{cases} XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind)} + CH_2XY, \\ X'Y'C{=}CH{-}CHXY \text{ (the product of the 2nd kind)} + CH_2XY, \\ XYC{=}CH{-}CHXY \text{ (the product of the 4th kind)} + CH_2X'Y'. \end{cases}$$

If the sodium atom is taken into consideration the relations are somewhat complicated, but fundamentally not altered. The above mentioned are the necessary processes for the formation of the four products; and the real condensations may include many other similar processes of addition and fission; nevertheless, more than the four products can never be expected. It is noteworthy that there are many chances for the more stable product to grow in amount in the cost of the less stable. It is remarkable that tetraethyl dicarboxyglutaconate having the largest groups attached to the central methenyl carbon atom was produced in many of the condensations[1] where it corresponded to any of the possible four kinds of products; and, therefore, it can not be said that the largest group is eliminated in the form of a methylene compound from the molecule of the intermediate methane triacetic acid derivative.

In the condensation in alcohol one product is prevalent. The reaction is of the homogeneous system, the materials and the products existing both in the dissolved state; and this facilitates the establishment of equilibrium, allowing the product the most table in the condition of that time to prevail. On the other hand, in the reaction in ether only one of the materials, the ethoxy-methylene compound, and none of the products, go into solution, and it is probable that various substances exist in various proportions in various places, and this permits many of the possible products to survive.

The fact that two isomeric compounds which differ from each other only in the position of the double union, and consequently of the sodium atom, the best example being diethyl *α*-sodio-*γ*, *γ*-dicyano-propylene-*α*, *α*-dicarboxylate and diethyl *α*-sodio-*α*, *α*-dicyano-propylene-*γ*, *γ*-dicarboxylate, are distinctly different is incompatible with the normal theory of J. F. Thorpe, which was already rejected by the present author and others.[2]

(1) The synthesis of the esters of acetyl-propylene-carboxylic acids is included, the results of which will be published later.

(2) This Bulletin, **3** (1928), 205; R. Malachowski u. M. Maslowski, *Ber.*, **61** (1928), 2521; R. Malachowski, *Ber.*, **62** B (1929), 1323.

Further the present investigation has thrown light on some obscure points in the previous experiments. The fact that two isomeric derivatives of dicarboxyglutaconic acid which differ from each other only in the positions of the double union and the sodium atom always proved to be identical is nothing but that one of the two possible isomerides was more stable and formed exclusively, the present investigation indicating that sometimes the less stable form can be obtained by the condensation in ether.

Experimental Part.

It seems convenient to begin with describing some of the products, especially concerning the methods of separation and identification, for the same substances may appear in more than one reactions. The following are all the known substances, and new compounds will be described in the places where they are met for the first time.

Tetraethyl a, γ-dicarboxyglutaconate, $(C_2H_5OCO)_2C=CH-CH(COOC_2H_5)_2$. Its sodium derivative is sparingly soluble in cold water and imparts opacity to water probably owing to its partial hydrolysis. It can be recrystallised from alcohol. The free ester formed by the action of dilute hydrochloric or sulphuric acid on the sodium compound is a colourless oil, and is identified by elementary analysis. It requires C=54.51; H=6.72%.

Triethyl γ-cyano-α-carboxyglutaconate, $C_2H_5OCO(CN)C=CH-CH(COOC_2H_5)_2$. The sodium derivative is easily soluble in water, and its alcoholic solution gives violet colouration with ferric chloride. The free cyano-ester is an oil, requiring N=4.94%. It is easily transformed into diethyl *α, α'*-dioxypyridine-*β, β'*-dicarboxylate $C_{11}H_{13}O_6N$ requiring N=5.49% and melting at 199°.

The esters of α, γ-dicyanoglutaconic acid, ROCO(CN)C=CH-CH(CN)COOR. Their sodium derivatives are all fine needle crystals, easily soluble in hot water. The corresponding free cyano-esters can not be obtained, but instead of them their semihydrates are always formed. Dimethyl, diethyl, and one of the methyl ethyl compounds have been obtained. The semihydrates are all yellow crystalline substances and can be identified by analysis and melting points.

Dimethyl compound:	$(C_9H_8O_4N_2)_2 \cdot H_2O$,	[225°]	N=12.90%;
Methyl ethyl compound:	$(C_{10}H_{10}O_4N_2)_2 \cdot H_2O$,	[197°]	N=12.12%;
Diethyl compound:	$(C_{11}H_{12}O_4N_2)_2 \cdot H_2O$,	[183°]	N=11.43%.

Further the diethyl compound gives a picrate of formula $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$ melting at 196-197°.

Diethyl γ,γ*-dicyano-propylene-*α,α*-dicarboxylate*, $(CN)_2C=CH-CH(COOC_2H_5)_2$. The sodium derivatite is easily soluble in water. On acidifying its aqueous solution an oily substance is precipitated. This is the free cyanoester, but after a short time it changes into colourless crystals of diethyl γ,γ-dicarbamyl-propylene-α,α-dicarboxylate $(NH_2CO)_2C=CH-CH(COOC_2H_5)_2$ which melts at 139-140°, changing opaque on prolonged heating. The free cyano-ester dissolved in alcohol changes into diethyl γ-cyano-γ-carbamyl-propylene-α,α-dicarboxylate $NH_2CO(CN)C=CH-CH(COOC_2H_5)_2$ melting at 212°.

Ethyl α,γ,γ*-tricyano-propylene-*α*-carboxylate*, $(CN)_2C=CH-CH(CN)COOC_2H_5$. The free cyano-ester can not be obtained, but the semihydrate $(C_9H_7O_2N_3)_2\cdot H_2O$ melting at 190° and requiring N=21.21%.

$\alpha,\alpha,\gamma,\gamma$*-Tetracyano-propylene*, $(CN)_2C=CH-CH(CN)_2$. This compound can be isolated only in its sodium derivative, which crystallises in needles from the aqueous solution. The aqueous solution produces no precipitation on acidifying, and if the aqueous solution acidified with hydrochloric acid is evaporated up in vacuum in the desiccator furnished with sulphuric acid and soda-lime, the crystals of the original sodium compound can be recovered. On adding a silver nitrate solution to the aqueous solution of the sodium compound a white precipitate is produced which is insoluble in dilute nitric acid.

Experimental Procedure. The first course of the reactions is to prepare the sodium derivatives of the methylene compounds. The sodium derivative of diethyl malonate was prepared by adding an excess (ten percent more than the theoretical quantity) of this ester to finely granulated metallic sodium covered with a large amount of pure ether. When the evolution of hydrogen is over and sodium disappears, the reaction is completed, and a paste of diethyl sodio-malonate is obtained.

Methyl sodio-cyanoacetate is prepared similarly, except that a small quantity of methyl alcohol is added to accelerate the reaction, and after the reaction is completed the solid is collected, dried in vacuum over sulphuric acid, weighed, and mixed with pure ether.

Ethyl sodio-cyanoacetate is prepared by adding the free ester to an alcoholic solution of sodium ethylate, the white crystals being collected, washed with pure ether, and well dried in vacuum. Sodio-malonitrile is prepared similarly.

In every case the sodio-methylene compound is mixed with pure ether and the calculated amount of the ethoxymethylene compound is added gradually under constant stirring. The reaction mass is from pale yellow to dark red. After standing for a length of time, the solid is separated

from ether by filtration or by dissolution in water. Then the solid or the aqueous solution is subjected to the process of separation and identification.

(1) *Condensation of ethyl ethoxymethylene-cyanoacetate with methyl sodio-cyanoacetate.* The semihydrate of the free cyano-ester obtained from the crude condensation product melted at 193°. Then the crude sodium compound was recrystallised four times from water, and the purified substance was transformed into the semihydrate, the latter being recrystallised once from absolute alcohol. It melted at 190°. Anal. Found: N=12.06, 12.23%. Nevertheless, this specimen is not identical with the already known methyl ethyl dicyanoglutaconate semihydrate, because there is a remarkable difference not only in the melting points, but also in the solubilities in absolute alcohol, the already known compound being insoluble in boiling alcohol while the new tolerably soluble in hot alcohol.

The author believes that the crude product was a mixture of the two isomeric methyl ethyl sodio-dicyanoglutaconates, and the specimen melting at 193° was the corresponding mixture of the semihydrates. The substance obtained by recrystallisation of the crude sodium compound was one of the isomerides, and that different from the already known.

(2) *Condensation of methyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate.* The specimen of the semihydrate obtained from either the crude or the recrystallised sodium compound melted at 196°. It can be said that the product was pure and unique; and, therefore, it is very natural to consider it the product of the first kind, that is γ-methyl α-ethyl α-sodio-α, γ-dicyanoglutaconate.

The sodium compound obtained in condensation 1 and giving the semihydrate melting at 190° is the α-methyl γ-ethyl compound. The only product of the condensations in alcohol is the γ-methyl α-ethyl compound, for it gives the semihydrate with the higher melting point.

(3) *Condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanoacetate.* The yellow pasty mass obtained by the reaction was dissolved in water. After a short time a crystalline substance separated from the solution. This was identified with diethyl α-sodio-dicyanoglutaconate by its transformation into diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.52%.

On acidifying the aqueous solution filtered from the above crystalline substance two kinds of substances separated, one being crystalline and the other oily. The former was identified with diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.50%. Melting point: 183°. The latter was collected by dissolving it in ether and evaporating the ethereal solution. On standing for three weeks the oil was partly changed into

crystals. The part which remained oily was purified by dissolving it in ether, extracting with a ten percent solution of sodium carbonate, acidifying the soda solution, extracting the oil with ether, and evaporating the dried ethereal solution. This was found to be nearly pure triethyl cyano-carboxy-glutaconate. Anal. Found: N=4.82%. Its alcoholic solution gave dark brown colouration with ferric chloride, which showed that the compound was triethyl γ-cyano-α-carboxy-glutaconate.[1] The crystalline part contained 5.71% of nitrogen and melted at 190–195°. It was probably diethyl α, α'-dioxy-pyridine-β, β'-dicarboxylate formed by the transformation of the triethyl cyano-carboxy-glutaconate.

(4) *Condensation of ethyl ethoxymethylene-cyanoacetate with diethyl sodio-malonate.* The crude mass obtained by the reaction was dissolved in water, and the aqueous solution was acidified with dilute hydrochloric acid. The whole was shaken with ether, and the ethereal and the aqueous solutions were treated separately.

The aqueous solution gave a small amount of a yellow crystalline substance. This was identified with diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.61%. Melting point: 183°.

The ethereal solution was shaken with a ten percent solution of sodium carbonate. The soda solution gave an enormous quantity of sparingly soluble solid, which contained 5.81% of nitrogen and seemed to consist mainly of diethyl α, α'-dioxy-pyridine-β, β'-dicarboxylate. The solid was digested with cold hydrochloric acid, washed, and dried. This was found to be the above pyridine derivative. Anal. Found: N=5.62%. Melting point: 199°.

The presence of alcohol in the mother liquor could be detected by its odour, indicating that the above pyridine derivative was formed from triethyl cyanocarboxyglutaconate according to the following equation:

$$C_{13}H_{17}O_6N + H_2O = C_{11}H_{13}O_6N + C_2H_5OH.$$

This triethyl cyanocarboxyglutaconate can be assumed to be the γ-cyano-α-carboxy-compound, that is the product of the first kind and more stable than the α-cyano-γ-carboxy-compound.

The mother liquor was acidified. The oily drops were collected, and transformed into a yellow crystalline sodium compound by shaking with a soda solution. This was identified with tetraethyl α-sodio-dicarboxy-glutaconate by the analysis of the free ester obtained from it. Anal. Found: C=54.60; H=6.74%.

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(1) Cf. this Bulletin, **3** (1928), 221.

(5) *Condensation of diethyl ethoxymethylene-malonate with sodio-malonitrile.* The condensation mass was dissolved in water. Crystals separated from the aqueous solution. These crystals and the mother liquor were treated separately.

The crystalline sodium compound was recrystallised from alcohol. Its alcoholic solution gave reddish violet colouration with ferric chloride. On acidifying its aqueous solution it was transformed into a colourless crystalline substance, which was identified with diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate by its melting point. Further the sodium compound could be transformed into diethyl γ-cyano-γ-carbamyl-propylene-α, α-dicarboxylate. Hence, it is diethyl α-sodio-γ, γ-dicyano-propylene-α, α-dicarboxylate.

The aqueous mother liquor filtered from the above crystalline sodium compound was acidified, and shaken with ether. The two liquid layers were treated separately.

On evaporating the ethereal solution a small amount of oil was obtained, which was then transformed into a crystalline sodium compound by shaking with a soda solution. This was probably tetraethyl α-sodio-dicarboxy-glutaconate, but the substance was not sufficient in purity and quantity for analysis.

It was expected that the aqueous solution might contain sodio-tetracyano-propylene. It was evaporated to a brown mass in vacuum over sulphuric acid and soda-lime. The brown mass was digested with alcohol, and the alcoholic solution was evaporated in vacuum to a crystalline mass. This was recrystallised twice from a small amount of water, animal charcoal being used to decolourize the solution. In this way nearly colourless needle crystals of a sodium compound were obtained. This substance resembles the sodium derivative of tetracyanopropylene as regards the properties, so that it was considered to be the expected substance until it was analysed. Anal. Found: N = 10.6%. The nitrogen content is equal to that of diethyl α-sodio-γ, γ-dicyanopropylene-α, α-dicarboxylate (N=10.9%), but the properties unequal, the new sodium compound being apparently unchangeable by acidifying its aqueous solution, just as same as sodio-tetracyano-propylene. The compound in question, therefore, can be nothing but diethyl α-sodio-α, α-dicyano-propylene-γ, γ-dicarboxylate $(C_2H_5OCO)_2C=CH-CNa(CN)_2$, the product of the first kind of this condensation.

(6) *Condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate.* The condensation mass was dissolved in water and the solution was acidified. Most of oil which separated out changed into colourless crystals after a short time, but among them some brown oil drops remained. The crystalline part was collected, washed with water, and then with ether,

the oily part being collected in the wash ether. The crystalline substance, the ethereal solution, and the aqueous mother liquor were treated separately.

The crystalline substance was identified with diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate. Hence, the original sodium compound is diethyl α-sodio-γ, γ-dicyano-propylene-α, α-dicarboxylate.

The ethereal solution gave an oil on evaporation. It was then transformed into a yellow crystalline sodium compound by shaking with a soda solution. This was identified with tetraethyl α-sodio-dicarboxyglutaconate by the analysis of the free ester obtained from it. Anal. Found: C=54.38; H=6.75%.

The aqueous mother liquor was expected to contain diethyl α-sodio-α, α-dicyanopropylene-γ, γ-dicarboxylate or more possibly sodio-tetracyano-propylene. But only a crystalline substance containing about 16% of nitrogen was isolated. It was probably a decomposition compound of either of them.

(7) *Condensation of ethyl ethoxymethylene-cyanoacetate with sodio-malonitrile.* The condensation seemed not to take place at the ordinary temperature, for on mixing these substances in pure ether no apparent change was observed. The mixture was heated for some time, and after evaporating most of ether it was kept at the room temperature for some ten days. Then the solid was dissolved in water and the aqueous solution was acidified, when dark brown oil separated out, which was extracted with ether.[1] From the ethereal solution, on drying with calcium chloride, yellow crystals separated. Anal. Found: N=18.95%. It seemed to be a mixture of ethyl tricyanopropylene-carboxylate semihydrate and diethyl dicyanoglutaconate semihydrate. Then it was recrystallised from alcohol. Anal. Found: N=17.41%. After recrystallisation the nitrogen content decreased, indicating that a mixture was being handled. It was easily found that the mixture contained diethyl dicyanoglutaconate semihydrate, for the alcoholic mother liquor of the above recrystallisation gave the characteristic picrate. The authentic specimen of ethyl α, γ, γ-tricyano-propylene-α-carboxylate semihydrate gives no product with picric acid. Another component of the mixture is believed to have been ethyl α, γ, γ-tricyanopropylene-α-carboxylate semihydrate, its mother substance being ethyl α-sodio-α, γ, γ-tricyanopropylene-α-carboxylate, the product of the second kind of this condensation. If it were the product of the first kind,

(1) None of the nitrile-esters of dicarboxyglutaconic acid which give semihydrates has ever separated in the form of oil, the present case being the only exception; but it can be considered that the separation of oil was due to the presence of malonitrile which would be formed from the sodio-malonitrile.

ethyl α-sodio-α, α, γ-tricyano-propylene-γ-carboxylate, it would be stable to acid, for the two known α-dicyano compounds are so.

(8) *Condensation of ethoxymethylene-malonitrile with ethyl sodio-cyano-acetate.* The crude product was purely white. On acidifying its aqueous solution a yellow crystalline substance was obtained, which was found to be nearly pure ethyl α, γ, γ-tricyanopropylene-α-carboxylate semihydrate. Anal. Found: N=20.72, 20.75%. The only product is, therefore, ethyl α-sodio-α, γ, γ-tricyano-propylene-α-carboxylate, the product of the first kind.

Summary.

From the results of eight reactions it was deduced that the four compounds,

$$XYC{=}CH{-}CNaX'Y',$$
$$X'Y'C{=}CH{-}CNaXY,$$
$$X'Y'C{=}CH{-}CNaX'Y',$$
$$XYC{=}CH{-}CNaXY,$$

can be produced in the condensation of the ethoxymethylene compound $XYC{=}CHOC_2H_5$ with the sodio-methylene compound $CHNaX'Y'$, where each of X, X', Y, and Y' represents either -CN or $-COOC_2H_5$.

The author expresses his hearty thanks to Prof. Matsubara for his kind inspection of this paper.

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RÖNTGEN ANALYSIS OF COPPER AMALGAMS.

By Nobuyuki KATOH.

Received November 18, 1929. Published January 28, 1930.

In the author's previous paper[1] the following results were published:

(1) The solid phase existing in high mercury amalgams has γ structure[2] and the lattice dimention is a=9.401Å.

(2) The solid phase prepared by squeezing high mercury amalgams under high pressures has the dimention just described.

(3) The upper copper limit of the homogenity range of the γ phase lies somewhere between 27.1-29.9 weight per cent of copper.

(1) N. Katoh, *Z. physik Chem.*, [B] **6** (1920), 27. see errata, V. 5, P. 306

(2) See Westgren and Phragmen, *Phil. Mag.*, [6] **50** (1925), 311.

(4) High copper amalgams consist in copper and the γ phase at ordinary temperature.

The samples used in the present investigation were prepared at the Minerallogical Institute in Oslo.[1]

For the powder photograms the Cr-K-radiation were used from a tube of the Siegbahn type, which was run with about 45 kilo-volts and 7.5ma. All cameras were designed by Dr. Phragmen.[2] The powder photograms were taken with three cameras of the focussing type, covering whole diffraction range. The cameras were calibrated with sodium chloride. The exposure time varied 5 to 9 hours. All the dimention values based on the length 5.6280Å for the edge of the elementary cube of the sodium chloride.

The photograms were rather weak by want of the practice of handling cameras. The result of the measurement and calculation was shown in the Table 1 and confirmed the former view.

In the case of a good photogram on which every line can be measured accurately, the determination of the lattice dimention may be carried out by means of the most deviated interferences.[3] The figures from each interference agree very well and it needs not farther calculation. But it is reasonable to take all the interferences when the photogram was weak.

The author used three photograms taken by the different cameras for determination of the γ phase. Taking $\mathrm{tg}^2\vartheta$ as the weight of the each observation of the interference lines, the constant χ in the equation $\sin^2\vartheta = \chi\ (h^2+k^2+l^2)$ calculated for each photogram by the following formura.[4]

$$\chi = \frac{\Sigma \chi \,\mathrm{tg}^2\vartheta}{\Sigma \,\mathrm{tg}^2\vartheta}\ , \qquad \Delta\chi = \pm\sqrt{\frac{\Sigma[(\chi-\chi_0)\,\mathrm{tg}\,\vartheta]^2}{(n-1)\Sigma\,\mathrm{tg}^2\vartheta}}$$

For the photogram taken by camera 5, $\chi = 0.01481 \pm 0.00001$
,, ,, ,, ,, ,, 6, $\chi = 0.01475 \pm 0.00003$
,, ,, ,, ,, ,, 8, $\chi = 0.01478 \pm 0.00001$

Then the most probable value of the constant was found by taking the weighted mean of the three figures as follows.

$$\chi = 0.01479 \qquad (\text{for } \mathrm{Cr}-\mathrm{K}_\alpha)$$

and the dimention of the γ phase is

(1) N. Katoh, loc. cit.
(2) Westgren and Phragmen, loc. cit.
(3) G. Hägg, Dissertation, 5, 1929 (Uppsala).
(4) E. Broch, *Z. physik. Chem.*, **127** (1927), 452.

$a=9.399\,\text{Å}$

$a=9.401\,\text{Å}$ (by Debye cameras)[1]

Tammann[2] observed the existence of the α phase by the thermal analysis but the present author could not find it in the specimens tempered at 100°C. for 48 hours. The powder photograms of a 70.5% Cu amalgam quenched at 380°C, and pure copper tempered at 100°C. taken with the same camera were compared. All the copper lines agree very well, so that the existence of α phase at this temperature is doubtful one but it needs farther investigation to settle this question.

Table 1.

Cr. Radiation. Cu—Hg (24.1% cu).

Intensity	Radiation	$h\,k\,l$	$\text{Sin}^2\frac{\vartheta}{2}\cdot 10^4$	$((h^2+k^2+l^2)/10^5$
w	β	310	1231	10.1231
s	α	310	1482	10.1482
w	β	321	1722	14.1230
$v\,w$	α	322	1777	12.1481
s	α	321	2072	14.1480
m	β	330,411	2246	18.1248
s	α	330,411	2660	18.1478
$v\cdot w$	β	332	2730	22.1241
$v\,w$	α	332	3238	22.1472
w	α	442,600	5336	36.1482
w	β	622	5402	44.1228
m	α	532,611	5616	38.1478
m	$\alpha+\beta$	631	5669	46.1233*
$v\,w$	β	444	5870	48.1223
$v\,w$	β	543,550,710	6099	50.1220
$v\cdot w$	α	541	6187	42.1473
m	α	622	6504	44.1478
m	α	631	6787	46.1475
s	α	444	7081	48.1475
m	α	543,550,710	7361	50.1472
w	α		7762	*
s	α_1	552,633,721	7981	54.1478
w	α_2	552,633,721	8010	54.1483
$v\,w$	β	811,741,554	8123	66.1231
w	α	642	8326	56.1483
w	α_1	651,732	9126	62.1471
w	α_2	651,732	9160	62.1478

* Extra lines.

(1) W. Katoh, loc. cit.

(2) G. Tammann and Th. Stassfurth, *Z. anorg. Chem.*, **143** (1925), 357.

Cr $K\alpha_1$ = 2.2848Å $\sin^2\vartheta = 0.01479\,(h^2+k^2+l^2)$ for CrKα

Cr $K\alpha_2$ = 2.2890Å $a = 9.399$Å

Cr $K\beta$ = 2.0805Å

Cr $K\alpha$ = 2.2862Å

Finally, the author desire to thank Professor A. Westgren, Ph.D., whok indly allowed him to carry out this work at the Röntgen Laboratory in the Stockholm Högskola.

October 25, 1929.

University of Stockholm,
Sweden.

ÜBER DIE OXYDATION KATHODISCH REDUZIERTER CHROMSÄURELÖSUNGEN AN PLATINANODEN.

Von **Shiro TAKEGAMI.**

Eigegangen am 22. November 1929. Ausgegeben am 28. Januar 1930.

Wie Roudnick[1] in Bestätigung früherer Angaben von Erich Müller und F. Soller[2] mitteilt, ist bei der Elektrolyse wässriger Lösungen von Chromsäure die anodische Oxydation des kathodisch gebildeten dreiwertigen Chroms zu Chromsäure an Bleianoden gegenüber an Platinanoden stark begünstigt. An Platinanoden ist sowohl bei Stscherbakow und Essin[3] sowie bei Roudnick die Oxydation in Prozenten der Stromarbeit eine auffallend schwankende. So finden erstere z.B. in ihrem Versuch 1 in zeitlich aufeinanderfolgenden Werten 10.0%, 2.8% und 7%, Roudnick in seinem Versuch 2 4.6%, 3.3%, 0.0%, 0.0%, 4.9%. Bei letzterem bleibt also, wie man sieht, unter Umständen die Oxydation völlig aus. Diese Erscheinung führt der Autor darauf zurück, dass ähnlich wie an der Kathode auch an der Anode ein Diaphragma gebildet wird, welches das Cr(3) hindert, auf die Anode zu treffen. Er konnte in der Tat feststellen, dass letztere nach ihrem Gebrauche einen grüngelben Schimmer aufwies, der durch Behandlung mit verdünnter Salzsäure oder Natronlauge unverändert blieb, durch heisse Natronlauge aber unter Gelbfärbung dieser verschwand.

,, Besondere Versuche zeigten, dass ein solches Diaphragma auf der Platinanode bei der Elektrolyse reiner Chromsäure nicht entsteht, sondern

(1) *Z. Elektrochem.*, **35** (1929), 249.
(2) Ebenda, **11** (1905), 863.
(3) Ebenda, **33** (1928), 245.

nur, wenn sie Cr(3) enthält, woraus zu schliessen ist, dass es sicher hier—wie an der Kathode—um die Bildung eines chromsauren Chromoxydes handeln muss, deren Mechanismus allerdings hier weniger durchsichtig ist."

Roudnick hat sich bemüht, unter mannigfacher Variation der Versuchsbedingungen dieses Diaphragma zu vervollkommnen, um eine Elektrode herzustellen, die die anodische Oxydation völlig und sicher auf die Dauer zu unterbinden vermöchte, was ihm aber nicht gelang.

Meine eigenen Versuche bewegten sich in derselben Richtung. Nur glaubte ich, durch Wahl anderer Versuchsbedingungen eher zum Ziele zu kommen. Ist nämlich, wie Roudnick angibt, die Gegenwart von Cr(3) Bedingung für die Bildung des Diaphragmas, so ist es möglich, dass eine bestimmte Mindestkonzentration davon benötigt wird. Arbeitet man nun mit einer kathodischen Stromdichte, wie Roudnick, bei der metallisches Chrom abgeschieden wird, so ist die kathodische Reduktion wesentlich geringer als wenn man diese Stromdichte so wählt, dass sich kein Chrom abscheidet. Sie teilt sich zudem im ersten Falle noch in die Reduktion zu Cr(3) und zu Cr met., während im letzten Falle nur Cr(3) gebildet wird. Mit anderen Worten: Man kommt bei der Wahl kleiner Stromdichten ohne Chromabscheidung zu höheren Cr(3)-Konzentrationen. Es war mithin möglich, dass Roudnick, der dies nicht tat, keine für die Diaphragmenbildung hinreichende Cr(3)-Konzentrationen in seiner Lösung hatte. Bei meinen Versuche wurde also in erster Linie Wert darauf gelegt, die kathodische Stromdichte unterhalb der Grösse zu halten, bei der sich metallisches Chrom abscheidet. Im übrigen wurden sie in ähnlicher Weise wie die von Roudnick ausgeführt.

Der elektrolytische Trog bestand aus einem Glasbecher von 8 cm. Höhe und 5 cm. Durchmesser, der mit einem Gummistopfen verschlossen war. Dieser hatte eine Anzahl Bohrungen zur Durchführung der Elektroden und zur Ableitung der während der Elektrolyse entwickelten Gase. Diese wurden in der üblichen Weise in einem Gasfangrohr gesammelt und mit den aus einem dahinter geschalteten Knallgascoulometer in der gleichen Zeit entwickelten verglichen. Der Sauerstoff dieser Gase wurde durch Absorption in einer Kupferpipette bestimmt. Durch eine Bohrung des Stopfens war noch ein längeres Glasrohr bis auf den Boden des Bechers geführt, das für gewöhnlich aussen durch einen Stopfen verschlossen war, das aber im Bedarfsfalle dazu diente, nach Entfernung des Stopfens, den Elektrolyten so weit anzusaugen, dass die Anode aus der Lösung herausragte und mit dem Auge betrachtet werden konnte (um zu sehen, ob sich ein Überzug gebildet hatte).

Der Trog stand in einem Thermostaten, vermittels dessen die Temperatur auf 30°C. gehalten wurde. Die beiden Elektroden, die sich plan-

parallel gegenüberstanden, bestanden aus Platin. Verwendet wurden stets 100 c.c. 25%iger Chromsäurelösung. Damit an der Kathode überhaupt eine Reduktion stattfindet, ist es nötig, dass HSO_4-Ionen gegenwärtig sind. Bei den ersten Versuchen, bei denen 0.04 bis 0.05 gr. Na_2SO_4 auf 100 c.c. Lösung gelöst wurden, zeigte sich nur zu allem Anfang eine geringe Reduktion, die bald auf Null absank. Deshalb wurden die weiteren Versuche mit 0.2 gr., ev. mehr, Na_2SO_4 pro 100 c.c. angestellt.

Versuch 1.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.2 gr. Na_2SO_4.
Stromstärke: 0.368 Amp.
Stromdichten: $D_A = 0.05$ Amp/qcm; $D_K = 0.0124$ Amp/qcm.(1)
Temperatur: 30°C.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduction
	H_2	O_2	H_2	O_2		
8– 23	44.6	22.3	1.5	20.3	8.96	96.63
30– 50	59.6	29.8	1.8	28.2	5.36	96 98
59– 79	59.8	29.9	2.1	29.2	2.34	96.48
87–107	60.4	30.2	6.0	30.4	0.0	90.06
115–135	59.2	29.6	7.9	29.6	0.0	86.65
145–165	58.6	29.3	28.2	30.3	0.0	51.87

Nach jeder beendeten Gasanalyse wurde die Anode besehen; es konnte keinerlei Belag auf derselben entdeckt werden.

Aus diesem Versuch geht hervor, dass bei der hier stattfindenden starken Reduktion nur zu Beginn eine Oxydation beobachtet wird, die mit der Zeit auf Null zurückgeht. Dies konnte im Sinne obiger Vermutung auf die mit der Zeit steigende Cr(3)-Konzentration zurückgeführt werden. Ist, wie Roudnick annimmt, die Störung der Oxydation durch ein anodisches Diaphragma bedingt, so ist dieses in meinem Falle in keiner Weise zu erkennen. Der allmähliche Rückgang der Oxydation scheint darauf hinzudeuten, dass die Ausbildung desselben Zeit erfordert.

Wie der folgende Versuch zeigt, ist aber die *allmähliche* Ausbildung nur dann wahrnehmbar, wenn die Cr(3)-Konzentration noch nicht bis zu einer gewissen Höhe angewachsen ist. Bei diesem Versuche wurden nämlich zwei gleiche Anoden (a) und (b) in den elektrolytischen Trog eingebaut und zunächst mit (a) gearbeitet, bis die Oxydation auf 0% abgesunken war. Dann wurde schnell (a) aus und dafür (b) eingeschaltet und unmittelbar weiter elektrolysiert. Dabei war an der Elektrode die Oxyda-

(1) Bei Berechnung der Stromdichte wurde nur *eine* Seite der Elektrode als vom Strom belastet angesehen.

tion sofort Null. Führt man also das Ausbleiben der letzteren auf ein Diaphragma zurück, so muss man annehmen, dass dieses bei Anwesenheit hinreichender Mengen Cr(3) sich sofort bildet.

Versuch 2.

Versuchsbedingungen des Vers. 1							
Anode	Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
		H_2	O_2	H_2	O_2		
a	5– 25	53.2	26.6	2.3	24.1	9.40	95.68
	30– 50	53.2	26.6	0.9	26.5	0.37	98.31
	55– 72	45.0	22.5	0.8	22.8	0.0	98.22
b	0– 20	58.6	29.3	0.8	29.4	0.0	98.64
	24– 44	58.6	29.3	0.7	29.7	0.0	98.82
	49– 69	58.2	29.1	0.6	29.2	0.0	98.97
	73– 93	57.4	28.7	0.6	28.6	0.0	98.96
	98–118	58.6	29.3	0.5	29.3	0.0	99.15

Auch bei diesem Vers. 2 konnte keine Veränderung der Anode wahrgenommen werden. Jedenfalls erkennt man aber, dass bei hoher kathodischer Reduktion und damit verbundener hoher Cr(3)-Konzentration in der Tat die anodische Oxydation verschwindet.

Der folgende Versuch 3 wurde längere Zeit fortgesetzt, um zu sehen, wie sich die Verhältnisse bei andauernder Anreicherung des Cr(3) gestalten.

Versuch 3.

Versuchsbedingungen wie bei Vers. 1						
Min. nach Beginn	Coulometer		Zellengas		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
8– 28	53.8	26.9	1.7	24.8	7.81	96.84
33– 53	53.8	26.9	1.1	27.1	0.0	97.96
56– 76	53.6	26.8	0.6	27.0	0.0	98.88
79– 99	53.6	26.8	2.8	27.2	0.0	94.78
102–122	53.8	26.9	7.5	27.2	0.0	86.06
124–144	53.6	26.8	9.0	27.0	0.0	83.21
146–166	54.0	27.0	29.2	27.0	0.0	45.93
170–190	53.4	26.7	53.0	26.4	1.44	0.75
194–214	53.6	26.8	53.0	26.0	2.98	1.12
218–238	53.2	26.6	53.2	25.4	4.72	0.0
242–262	53.2	26.6	52.8	25.6	3.76	0.75
266–286	53.0	26.5	52.4	26.0	1.89	1.13
290–310	53.2	26.6	52.5	25.5	4.13	1.32
315–335	53.4	26.7	52.2	26.3	1.20	2.25

In diesem Versuche tritt uns die merkwürdige Erscheinung entgegen, dass die *Reduktion* nach einer länger andauernden Elektrolyse auf ganz kleine Werte herabgeht. Es liegt dies nicht an einer Verarmung an Chromsäure, denn die Analyse ergab einen Gehalt von 12.5 Cr(6) d. i. 24 gr. CrO_3 gegen 25 gr. zu Beginn und 0.5 gr. Cr(3). Es zeigt sich das auch darin, dass nach Unterbrechung der Elektrolyse und nach Fortsetzung derselben nach einer gewissen Pause die Reduktion wieder ihre anfänglich hohen Werte annimmt, um wieder innerhalb längerer Zeit nahezu zu verschwinden, wie aus Vers. 4 hervorgeht.

Versuch 4.

Fortsetzung der Elektrolyse von Vers. 3.						
Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
10– 30	52.8	26.4	1.2	24.5	7.2	97.73
33– 53	52.6	26.3	1.0	24.8	5.7	98.10
55– 75	53.0	26.5	1.4	26.4	0.38	97.36
79– 99	53.6	26.8	8.1	26.9	0.0	84.89
101–121	52.8	26.4	18.3	26.4	0.0	65.34
123–143	53.0	26.8	41.4	26.4	0.38	21.89
147–167	53.2	26.6	51.8	25.2	5.26	2.63
169–189	53.2	26.6	52.1	25.9	2.63	2.07
191–211	52.8	26.4	51.8	25.8	2.27	1.89
Elektrolyse 16 Stunden unterbrochen und wieder eingeschaltet						
10– 30	54.6	27.3	1.8	24.2	11.36	96.70
33– 53	54.2	27.1	1.0	24.8	8.49	98.10
56– 76	53.6	26.8	0.8	25.0	6.72	98.51
79– 99	53.0	26.5	0.6	24.8	6.54	98.87
102–122	53.6	26.8	0.5	24.8	7.46	99.07
125–145	52.8	26.4	0.8	25.2	4.54	98.49
147–167	51.8	25.9	17.5	24.6	5.02	66.21
170–190	52.6	26.3	45.6	25.4	3.42	13.31
192–212	52.0	26.0	50.3	23.9	8.08	3.27
217–237	52.4	26.2	51.3	24.7	5.72	2.10

Selbst nach dieser langen Dauer konnte von einer Verarmung an Chromsäure nicht die Rede sein, da noch 11.5 gr. Cr(6) d. i. 22.1 gr. CrO_3 vorhanden waren neben 1.5 gr. Cr(3).

Die Kathode erholt sich also gewissermassen immer wieder nach einer Ruhepause, um bei der andauernden Elektrolyse mit der Zeit reduktionsunfähig zu werden. Man kann das vielleicht so erklären, dass bei Gegenwart von Cr(3) im Elektrolyten das Diaphragma auf der Kathode, welches nach E. Müller aus chromsaurem Chromoxyd besteht, sich mit der Zeit so verdickt, dass das HSO_4'-Ion nun nicht mehr bei Potentialen unterhalb der Wasserstoffentwicklung hindurchgezogen und dadurch seine die Reduktion hervorrufende Wirkung vernichtet wird.[1] Wird der Strom unterbrochen, dann wird dieser Überzug gelöst und bedarf nun wieder einer gewissen Zeit, um sich zur hinreichenden Dicke auszubilden. Die Länge dieser Zeit hängt vermutlich von äusseren Umständen ab und dürfte grösser sein, wenn gerührt wird, was allerdings erst untersucht werden müsste, weil ja an sich von dem Zeitpunkte an, wo die Reduktion verschwindet, durch die nun heftigere Wasserstoffentwicklung eine verstärkte Rührung gegeben ist.

Was nun die Oxydation anbetrifft, so fällt es auf, dass dieselbe von dem Moment, wo die Reduktion verschwindet, bei Vers. 3 wieder in Erscheinung tritt. Später bei der Fortsetzung der Elektrolyse in Vers. 4 wird sie nur noch einmal Null und ist im übrigen recht unregelmässig. Da bei Vers. 3 nach der 166 Minute die Reduktion nahezu Null ist, so ist für die folgenden Stadien auch die Cr(3)-Konzentration nahezu konstant. Wenn trotzdem die Oxydationswerte schwanken, so gewinnt man den Eindruck, dass die Cr(3)-Konzentration für die anodischen Verhältnisse nicht allein massgebend ist. Um zu sehen, ob vielleicht die Konzentration des Na_2SO_4 einen Einfluss hat, wurden noch 2 Versuche, 5 und 6, mit Erhöhung derselben angestellt.

Versuch 5.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.5 gr. Na_2SO_4
Stromstärke, Stromdichten und Temperatur wie bei Vers. 1.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
6 – 26	58.8	29.4	2.5	25.3	13.95	95.75
34 – 54	58.4	29.2	1.3	28.5	2.40	97.79
64 – 84	57.2	28.6	1.0	27.0	5.59	98.25
95–115	57.8	28.9	1.4	26.0	10.04	97.58
125–145	58.8	29.4	1.8	27.3	7.14	96.94
154–174	58.4	29.2	2.4	27.3	6.51	95.89

(1) E. Müller und O. Essin, *Z. Elektrochem.*, **35**, Heft 12.

Versuch 6.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 1.0 gr. Na_2SO_4
Stromstärke, Stromdichten und Temperatur wie bei vorigem Vers.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
5— 25	59.4	29.7	2.2	25.9	12.99	96.30
33— 53	57.8	28.9	1.6	27.2	5.88	97.23
62— 82	59.4	29.7	1.0	28.8	3.03	98.31
90—110	59.0	29.5	1.0	29.0	1.69	98.31
118—138	59.4	29.4	1.1	28.9	1.70	98.15

Wenn man auch aus Vers. 5 den Eindruck gewinnt, dass die Erhöhung der Na_2SO_4-Konzentration von 0.2 auf 0.5 gr./100 c.c. gegenüber Vers. 3 die Oxydation erhöht, so wird er doch durch Vers. 6, wo 1 gr. Na_2SO_4 verwendet wurde, wieder verwischt, indem hier die Oxydation nicht noch weiter steigt, sondern wieder absinkt, und sie zudem wieder grosse Schwankungen zeigt.

Schliesslich wurden noch 2 Versuche, 7 und 8, mit kleinerer anodischer Stromdichte angestellt, bei denen auch der Gehalt an Na_2SO_4 verschieden war.

Versuch 7.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.2 gr. Na_2SO_4
Stromstärke: 0.067 Amp.
Stromdichten: $D_A = 0.01$ Amp/qcm; $D_K = 0.00226$ Amp/qcm.
Tem.: 30° C.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
10— 80	44.6	22.3	2.6	18.6	16.60	94.17
84—154	44.0	22.0	6.8	21.0	4.55	98.18
157—227	43.6	21.5	0.4	21.4	0.48	99.07
mit neuer Anode fortgesetzt						
13— 83	43.0	21.5	0.8	20.8	3.26	98.14
86—156	43.0	21.5	0.4	21.1	1.89	99.07

Versuch 8.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 1.0 gr. Na_2SO_4
sonst wie bei vorigem Versuch.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
17– 77	38.4	19.2	2.1	15.6	18.75	94.53
80–150	43.8	21.9	1.0	20.5	6.39	97.13
154–224	43.8	21.9	0.8	21.0	4.29	98.18
229–299	43.6	21.8	0.6	21.0	3.67	98.62
231–318	53.8	26.9	0.5	26.7	0.74	99.07

Bei der geringeren anodischen Stromdichte kommt ebenfalls die Oxydation mit der Zeit auf Null, nur dauert es längere Zeit. Ob sie sich nun hier für längere Zeit auf Null hält oder wie bei Vers. 3/4 später wieder ansteigt, wurde wegen der infolge der geringen Stromstärke benötigten ausserordentlich langen Zeit nicht untersucht.

Bei allen bisher angeführten Versuchen war an der Kathode kein Chrom abgeschieden worden. Es wurde deshalb noch einer angestellt, bei dem dieses der Fall war.—Vers. 9.

Versuch 9.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.2 gr. Na_2SO_4.
Stromstärke: 0.336 Amp.
Stromdichten: $D_A = 0.05$ Amp/qcm; $D_K = 0.20$ Amp/qcm.
Temp.: 30° C.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
7– 27	53.8	26.9	32.0	25.8	3.99	40.52
29– 49	52.8	26.4	34.2	26.4	0.0	35.23
52– 72	52.8	26.4	35.4	26.0	1.51	32.96
75– 95	53.2	26.6	36.4	25.9	2.63	31.58
97–117	52.4	26.2	36.4	25.2	3.82	20.53
120–140	52.6	26.3	37.6	25.1	4.56	28.14
143–163	52.6	26.3	37.8	25.1	4.56	28.49
166–186	53.0	26.5	37.9	25.5	3.77	29.49
188–208	52.6	26.3	38.1	25.5	3.04	29.46
211–231	52.6	26.3	38.4	25.5	4.94	27.00

In Vers. 9 haben wir ähnliche Verhältnisse wie Roudnick. Die Stromausbeute an metallischem Chrom betrug 18.5%, die durchschnittliche Reduktion 30.6%, sodass nur 12.1% auf die Bildung von Cr(3) entfallen. Wenn auch die Oxydation hier im Durchschnitt grösser ist als in Vers. 1, so kann man dies doch nicht ohne weiteres im Sinne der eingangs geäusserten Vermutung deuten, dass nämlich die höhere Cr(3)-Konzentration bei letzterem Versuche daran Schuld ist, weil gerade in den Anfangsstadien des Vers. 9 die Oxydation ganz erheblich kleiner ist als in Vers. 1, während doch die Cr(3)-Konzentration entsprechend den Reduktionsprozenten (auf Cr(3) berechnet) dort 12%, hier 96%, bei Vers. 9 wesentlich kleiner sein muss. Vielmehr muss man im Hinblick auf die ausserordentlichen Schwankungen in den Oxydationswerten eingestehen, dass die Erscheinungen an der Anode von noch unerkannten Faktoren bestimmt werden.

Trotzdem ich bei keinem meiner Versuche irgend eine Änderung der Anode erkennen konnte, neige ich doch auch zu der Ansicht, die Roudnick ausgesprochen hat, dass eine Filmbildung auf der Anode eine Rolle spielt. Schwer ist sonst die bei fast allen meinen Versuchen zu beobachtende Abnahme der Oxydation in den ersten Stadien der Elektrolyse, die besonders deutlich bei den geringen anodischen Stromdichten der Vers. 7 und 8 in Erscheinung tritt, zu deuten. Denn da es sich um eine Oxydation des Cr(3) handelt, so sollte man normalerweise eine Steigerung derselben mit der Zeit erwarten, da mit dieser auch die Cr(3)-Konzentration wächst. Ein Zusammenhang zwischen dieser und den Oxydationswerten ist aber nirgends zu erkennen. Möglicherweise sind die schwankenden Daten der letzteren darauf zurückzuführen, dass der Film durch die Sauerstoffentwicklung verletzt wird und dass deren Wirkung von unkontrollierbaren Umständen abhängt.

Wenn es mir nicht gelungen ist, wie Roudnick eine mit einem sichtbaren Überzug versehene Anode zu erhalten, mag das vielleicht dem Umstande zuzuschreiben sein, dass ich bei einer um 10° tieferen Temperatur gearbeitet habe. Möglicherweise bringt das Studium des Einflusses der Temperatur auf die anodischen Erscheinungen uns der Lösung der interessanten Fragen näher.

Herrn Prof. Dr. Erich Müller danke ich für die Anregung zu dieser Untersuchung und für seine Unterstützung.

Juli 1929.

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ON THE THERMAL DECOMPOSITION OF ALIPHATIC ETHERS.

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The ether has hitherto been considered to be stable to chemical reagents and to heat.[1] But the nature of the ether has not yet been made clear, as the chemistry of ether has advanced little. Recently S. Komatsu and his co-workers are exploiting the field of the chemistry.[2] The writer made some experiments on the thermal decomposition of aliphatic alcohols,[3] concluding that the alcohols are decomposed into corresponding olefines through the stages of the corresponding ethers: $R.CH_2OH \rightarrow (R.CH_2)_2O + H_2O \rightarrow R':CH_2 + H_2O$. For introducing the conclusion, the writer proved that the corresponding ethers were formed and that the thermal effects of ether-formation were always larger than those of other possible cases.

It will however be proper to discuss the problem with the result of the thermal decomposition of the corresponding ethers under the same conditions. On one side for above purpose and on the other for obtaining some data for making clear the nature of the ether, especially for getting some idea on the affinity of alkyl groups to oxygen, the writer made the present experiments as works on the field are found scarcely in the chemical literature.

In 1835, J. Liebig[4] observed that ethyl ether was decomposed into aldehyde, a burnable gas and water when its vapour was passed through a heated glass tube filled with glass pieces and the formation of acetylene in the reaction was also observed.[5] W. Tischtschenko[6] reported that the ether was mainly decomposed into aldehyde and paraffines when heated at high temperature, unsaturated hydrocarbons, carbon monoxide and hydrogen being also produced. On passing ethyl ether through a tube filled with pumice or a mixture of pumice and zinc dust at about 500°, Nef[7] observed the formation of ethylene, carbon monoxide, hydrogen,

(1) V. Meyer und P. Jacobson, "Lehrbuch der organischen Chemie," I-1, 289, (Leipzig: Veit & Comp.), 1907; J. B. Sendrens, *Compt. rend.*, **146** (1908). 1211; J. Houben, "Die Methoden der organischen Chemie," III, 136 (H. Meerwein), (Leipzig: Georg Thieme.), 1923.
(2) Private communication.
(3) This Bulletin, **4** (1929), 177.
(4) *Ann.*, **14** (1835), 134.
(5) M. Berthelot, *Ann.*, **116** (1860), 117.
(6) *Chem. Zentr.*, (1900) I, 586
(7) *Ann.*, **318** (1901), 198.

methane and ethene with a small amount of acet- and croton-aldehydes Under high temperature and pressure, ethyl ether was decomposed into ethylene and water in the presence of iron and alumina[1]; the same decomposition occurred at 200-300° in contact with alumina.[2] When ethyl ether was passed through a heated platinum tube, the principal change was the formation of ethane and acetaldehyde accompanied by ethylene and water[3]. But ethyl ether in gaseous state, when heated at about 500° in a silica bulb without catalyst, did not decompose according to the formula, $C_2H_5 \cdot O \cdot C_2H_5 = 2C_2H_4 + H_2O$, but carbon monoxide separated from the molecule, the net result being thus: $CO + 2CH_4 + 0.5C_2H_4$.[4] Ethyl ether gave ethyl alcohol when heated with alumina under ordinary pressure[5] or when treated with silicon tetrachloride[6] or with disilicon hexachloride.[7]

Propyl ether behaved similar to ethyl ether when heated.[8] The thermal decompositions of dimethyl and di-isopropyl ether and some mixed ethers were studied to some extent.[9]

As the experimental materials, ethyl, *n*-propyl, *n*-butyl, *n*-amyl and ethyl-*n*-butyl ethers and *n*-amyl alcohol are used for making comparative studies.

The experiment was conducted under the same conditions, using the same apparatus and catalyst as in the case of the alcohol. Small grains of Japanese acid clay are filled into a hard glass tube and dried and activated at 350–400°. When the temperature of the catalyst attained a desired one, the sample is gradually dropped into one end of the tube at a definite rate. It is there evaporated and acted with the clay. The produced liquid and gas are collected into proper receivers and analysed. The gas is analysed by ordinary absorption method combining a combustion one for hydrogen and paraffines. As to the liquid product, water, alcohols, ethers and sometimes aldehydes are estimated by fractional distillation, by combining the action of toluene, sodamide and others. Alcohols are proved by the formation of their phenylurethanes or benzoylesters.

(1) W. Ipatieff, *Ber.*, **37** (1904), 2994; *Chem. Zentr.*, (1904), II, 1020.
(2) J. B. Sendrens, *Compt. rend.*, **146** (1908), 1211; *Bull. soc. chim.*, [4] **3** (1908), 823; C. J. Engelder, *J. Phys. Chem.*, **21** (1917), 698.
(3) E. Peytral, *Bull soc. chim.* [4] **35** (1924), 964.
(4) C. N. Hinshelwood, *Proc. Roy. Soc.* (London), [A] **114** (1927), 84.
(5) W. Ipatieff, loc. cit.
(6) F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, (1927), 2734.
(7) F. S. Kipping and R. A. Thompson, *J. Chem. Soc.*, (1928), 1989.
(8) W. Tischtschenko, loc. cit.
(9) C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc.* (London), [A] **115** (1927), 215; J. V. S. Glass and C. Norman *J. Chem. Soc.*, (1929), 1815; J. V. S. Glass and C. N. Hinshelwood, ibid., (1929), 1804.

When aliphatic ethers are passed over heated Japanese acid clay, they are decomposed into corresponding olefines, alcohols and water, small amounts of aldehydes, gaseous compounds, sometimes of esters and a kind of petroleum hydrocarbons (at high temperature) being also produced. A very small amount of free carbon is precipitated on the catalyst, the higher the temperature, the more the amount of carbon.

The mechanism of the thermal decomposition of aliphatic ethers in the presence of Japanese acid clay is assumed to be as follows:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}R = 2R{\cdot}CH : CH_2 + H_2O.$$

Figures on the succeeding pages show the mutual quantitative relations between the decomposition products at different temperatures from ethyl, propyl, butyl, amyl and ethyl-butyl ethers and amyl alcohol. That the ratios of olefines and water produced are almost constant (2 : 1) at above ca. 300° and that the yields of olefines from ethers are always larger than those from corresponding alcohols will explain the above reaction mechanism, i.e., two alkyl groups are split off from oxygen at the same time at the temperatures.

In the case of ethyl-butyl ether, the decomposition product is a mixture of ethylene, butylene, ethyl and butyl alcohols and water, where the amounts of butylene and ethyl alcohol being larger than those of ethylene and butyl alcohol. The affinity between butyl proup and oxygen is therefore weaker than that between ethyl group and oxygen: $C_2H_5 > C_4H_9$.

On the formation of alcohols at low temperature, the writer wishes to assume the following reaction:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}R = R{\cdot}CH : CH_2 + R{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

As mentioned before, the ether has hitherto been thought as a stable compound; this conception will be correct in a certain limit, but it will not be proper to assume it very stable. Not only by the action of acids, but also even by alkalies, it is decomposed, especially at elevated temperatures.

On the hydrolysis of the ether by acids, some works[1] have been recorded, the decomposition product being different according to the temperature, at which the ether is treated:

$$R{\cdot}O{\cdot}R' + HX \begin{cases} \nearrow RX + R'OH, \\ \rightarrow ROH + R'X, \\ \searrow RX + R'X. \end{cases}$$

(1) R. D. Silva, *Ann. chim. phys.*, [5] **7** (1876), 429; W. Lippert, *Ann.*, **276** (1893), 148; A. Michael. *J. prakt. Chem.*, [2] **64** (1901), 106, etc.

As the name indicates, the Japanese acid clay reacts acidic. The liquid products in the reactions are always acidic. When ethyl, propyl or butyl ether is heated in a sealed tube at 200–250° with water in the presence of the clay, corresponding alcohols are produced, the amount being however small. H. Inoue[1] observed the hydrolysis of acetic ester by passing it over Japanese acid clay at about 200°. And W. Ipatieff[2] reported the formation of ethyl alcohol by the thermal decomposition of ethyl ether under the influence of alumina. A. Skrabal and H. Airoldi[3] measured the saponification constant of ethyl ether under the influence of benzene sulphonic acid and S. K. Kulkarni Jatkar and H. E. Watson[4] calculated the equilibrium constant of the reaction, $C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2O \rightleftarrows 2C_2H_5OH$.

From these facts, there is a possibility to suppose that the alcohol is produced by the hydrolysis of the ether due to the special characteristics of the clay:

$$R{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}R + H_2O = 2R{\cdot}CH_2OH.$$

And it will of course be natural to suppose a very small amount of alcohol present in the liquid product is formed by the hydrolysis, but the saponification constant of Skrabal and Airoldi is only 9×10^{-5} at 98° and the equilibrium constant of Jatkar and Watson is 7.3 at 227°. Would the hydrolysis be permitted, the degree will be very small, while the amount of the alcohol determined is not small; the writer wishes therefore to propose the above reaction mechanism:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}R = R{\cdot}CH{:}CH_2 + R{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

As will be seen from the tables and diagrams the clay represents a special characteristics to the ether, the lower the temperature, the less the decomposition to the olefines, but larger the production of alcohols. At above ca. 300°, almost complete decomposition takes place rapidly i.e., at high temperature, almost all of the ether is decomposed into olefine and water.

As in the case of the alcohol, the amounts of the produced olefines increase with the rise in the reaction temperature, which is shown in Fig. 1. At above ca. 300°, the decomposition is extremely promoted. There is almost no difference between the amounts of the produced olefines according to the difference of the ether. In the case of ethyl ether, the rate of the formation of ethylene is slightly less than the cases of other ethers.

(1) Private communication; cf. this Bulletin, **1** (1926), 157.
(2) Loc. cit.
(3) *Monatsh. f. Chem.*, **45** (1924), 13.
(4) *J. Indian Inst. Sci.* [A] **9** (1926), 99; *Chem. Abstr.*, **21** (1927), 386.

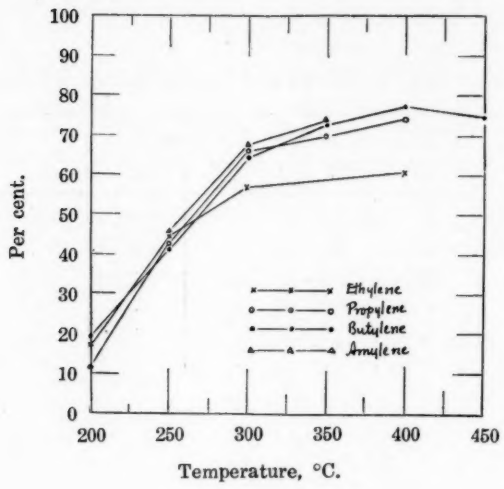

Fig. 1.

The double bond of the olefine produced belongs generally to the carbon atom linked with oxygen:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}R \rightarrow R{\cdot}CH : CH_2.$$

But in the case of butyl ether, butylene is a mixture of α-and β-isomers, the latter being predominated. And amylene produced from amyl alcohol and ether is also a mixture of α-compound ($CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH : CH_2$) and β-one ($CH_3{\cdot}CH_2{\cdot}CH : CH{\cdot}CH_3$); these will be produced by the migration of double bond by the further action of the heated clay for producing more stable isomers.

At low temperatures (mainly at 200–250°), corresponding alcohols are produced, the amount of which decreasing rapidly with the rise of temperature. Ester is produced in the case of ethyl ether, but not distinct in the cases of other ethers. Aldehyde is produced in small amounts at every cases. The amounts of carbon monoxide, hydrogen and aldehyde isolated are not large, the formation of aldehyde in the reaction will not therefore be large.

Ethyl Ether. Pure ethyl ether is used after distilling over metallic sodium, boiling point of which being 35°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 1, 2, 3 and 4, and the mutual relations of the main products are shown in Figs. 2 and 3.

Table 1.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %	Liquid yield %
				Liquid, gr.	Gas, L.		
33	73.4	200	0.35	40	11.65	16.4	54.5
34	58.3	200	0.34	28	9.87	18.6	48.0
35	87.1	250	0.34	21	39.09	50.5	24.1
36	104.4	250	0.34	29	36.22	38.4	27.8
37	126.0	250	0.33	32	58.73	53.2	25.4
38	117.4	300	0.33	25	61.49	58.8	21.3
39	118.8	300	0.32	27	63.86	55.1	22.7
40	86.4	400	0.34	19	47.57	59.0	22.0
41	104.8	400	0.35	22	56.16	62.6	21.0

Table 2.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
33	200	82.5	6.4	0.4	6.8	1.4	2.5
34	200	88.0	2.1	0.2	5.4	2.1	2.2
35	250	89.9	3.1	0.2	4.7	1.0	1.1
36	250	88.4	3.6	0.4	3.4	1.0	3.2
37	250	91.2	3.1	0.2	2.8	1.0	1.7
38	300	89.7	5.1	0.2	2.2	1.0	1.8
39	300	81.9	3.0	0.2	7.3	3.2	4.4
40	400	85.6	1.8	0.4	4.0	3.2	5.0
41	400	93.4	2.4	0.4	1.2	1.4	1.2

Table 3.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde	Ester
33	200	61.8	19.8	14.8	0.52	+
34	200	57.5	23.2	14.3	0.43	+
35	250	6.2	25.7	68.1	0.05	+
36	250	21.7	26.2	44.8	0.66	+
37	250	10.0	20.0	65.6	0.19	+
38	300	2.4	1.2	94.0	0.02	+
39	300	trace	4.1	92.6	0.02	+
40	400	0	0.5	97.4	0.02	−
41	400	0	0.3	95.5	0.01	-

Table 4.

Yields of the Main Substance, mol per cent.

No.	Reaction temp.	Ethylene	Ether	Alcohol	Water
33	200	43.4	33.3	17.2	33.3
34	200	49.6	28.0	17.8	28.0
35	250	133.6	1.7	10.2	67.2
36	250	101.5	7.7	12.1	51.1
37	250	140.6	2.4	8.2	68.8
38	300	155.3	0.6	0.4	82.7
39	300	145.4	trace	1.3	89.2
40	400	156.1	0	0.9	88.3
41	400	165.5	0	0.5	82.7

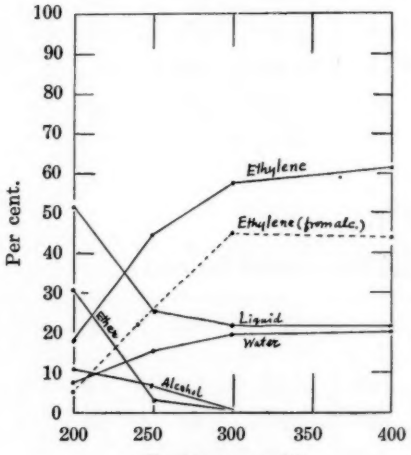

Fig. 2.

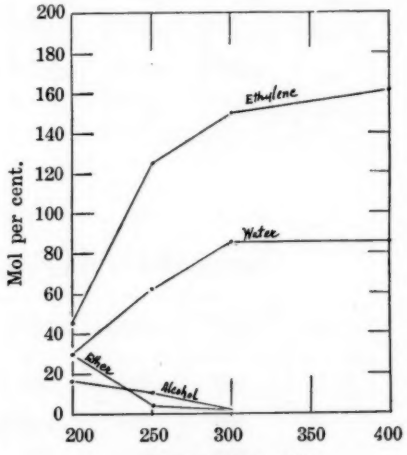

Fig. 3.

n-**Propyl Ether.** One part of the ether is prepared from n-propyl alcohol by the method of Kraft[1] and the other is Eastman's product. They are carefully purified by distilling over metallic sodium, boiling point of which being 90–91°. The experimental conditions, decomposition products and the analytical results of the products are tabulated in Tables 5, 6, 7, and 8, and the mutual relations of the main compounds are shown in Figs. 4 and 5.

(1) *Ber.*, **26** (1893), 2829.

Table 5.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temera-ture, °C.	Dropping rate of sample, gr./min.	Decomposition products		Propylene yield, %	Liquid, yield, %
				Liquid, gr.	Gas, L.		
42	46.0	200	0.31	33.0	2.52	9.2	71.7
43	46.0	200	0.31	30.5	4.38	13.9	66.3
44	46.0	250	0.31	20.0	10.81	41.5	43.5
45	46.0	250	0.31	20.0	10.99	43.2	43.5
46	46.0	300	0.31	8.5	16.49	65.2	18.5
47	46.0	300	0.31	8.7	17.52	68.5	18.9
48	46.0	350	0.31	8.0	17.98	67.2	17.4
49	46.0	350	0.31	8.4	18.17	70.8	18.3
50	46.0	400	0.31	8.0	18.63	73.3	17.4
51	46.0	400	0.31	8.5	19.47	75.2	18.5

Table 6.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
42	200	89.2	1.0	1.2	3.0	2.7	1.0
43	200	77.4	0.5	0.2	2.5	1.1	0.6
44	250	94.0	0.6	0.2	2.4	1.3	0.5
45	250	96.2	1.0	0.2	1.4	0.9	0.3
46	300	96.8	0.6	0.4	0.8	1.3	0.1
47	300	95.8	1.0	0.2	1.0	1.2	0.4
48	350	94.2	0.6	0	1.2	1.8	0.5
49	350	95.4	0.6	0.2	1.4	1.1	0.5
50	400	96.4	0.4	0.2	1.2	1.2	0.4
51	400	94.6	0.8	0.3	1.2	2.0	0.7

Table 7.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde
42	200	74.9	17.6	3.0	0.12
43	200	63.9	18.7	13.1	0.08
44	250	52.0	16.5	25.5	0.24
45	250	52.5	17.0	24.5	0.19
46	300	8.2	2.4	83.5	0.09
47	300	8.1	2.3	86.2	0.09
48	350	3.8	0.3	93.8	0.02
49	350	2.4	0.2	95.2	0.01
50	400	7.5	trace	90.0	0.02
51	400	3.5	trace	94.1	0.01

Table 8.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Propylene	Ether	Alcohol	Water
42	200	22.2	53.8	21.6	12.4
43	200	33.5	42.4	21.1	49.3
44	250	100.8	22.7	12.2	62.9
45	250	104.8	22.9	12.7	60.4
46	300	158.1	1.6	0.7	87.6
47	300	166.3	1.6	0.7	92.7
48	350	167.9	0.7	0.1	92.7
49	350	171.9	0.4	0.1	98.7
50	400	178.1	1.3	trace	88.9
51	400	182.5	0.7	trace	98.7

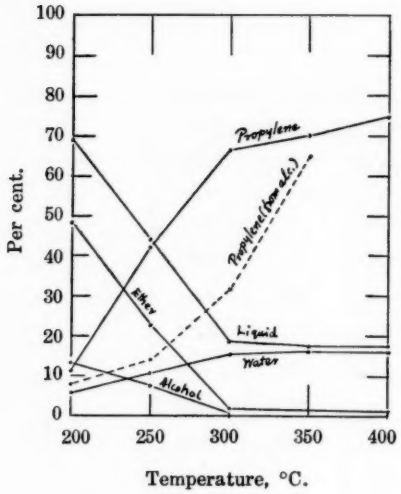

Fig. 4.

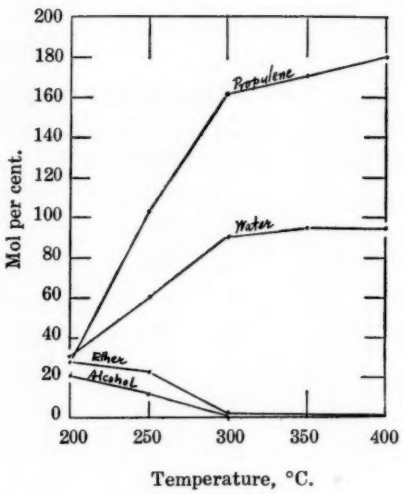

Fig. 5.

***n*-Butyl Ether.** Pure ether of Eastman Kodak Co. is used after distilling over metallic sodium, boiling point of which being 140–141°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 9, 10, 11 and 12, and the mutual relations of the main compounds are diagramed in Figs. 6 and 7.

Table 9.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Butylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
52	46.0	200	0.31	34.0	3.51	15.3	73.9
53	46.0	200	0.31	30.0	4.95	23.6	65.2
54	42.5	250	0.35	22.0	6.31	33.3	51.8
55	46.0	250	0.31	21.0	9.50	49.5	45.7
56	50.0	300	0.31	13.0	13.01	61.6	26.0
57	46.0	300	0.31	9.0	13.04	67.4	19.6
58	44.4	350	0.32	8.0	14.16	78.8	18.0
59	46.0	350	0.31	8.0	13.93	71.2	18.5
60	47.0	400	0.34	8.0	19.79	83.2	17.0
61	46.0	400	0.31	8.0	14.20	72 3	17.4
62	46.0	450	0.31	6.5	14.66	74.7	14.1
63	46.0	450	0.31	6.5	14.93	74.8	14.1

Table 10.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
52	200	80.0	1.2	1.0	2.8	2.7	8.2
53	200	87.8	1.6	1.2	2.4	1.5	4.1
54	250	89.7	0.4	0.8	2.0	3.0	4.1
55	250	95.6	1.8	0.5	0.2	0.8	1.1
56	300	94.5	0	0.4	3.1	0.7	1.3
57	300	95.0	1.4	0.2	1.0	1.0	1.4
58	350	93.7	3.1	0.2	1.0	0.5	1.5
59	350	94.0	0.8	0.4	1.6	0.8	2.4
60	400	78.9	2.8	0.6	2.8	2.6	8.6
61	400	93.6	0.4	0.6	1.8	1.0	2.2
62	450	93.6	0.8	0.6	1.2	1.3	2.6
63	450	92.0	0.6	0.8	1.4	1.5	3.7

Table 11.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde
52	200	73.2	15.3	5.9	0.05
53	200	70.0	11.3	8.0	0.06
54	250	47.7	6.4	15.5	0.05
55	250	69.5	13.3	17.1	0.06
56	300	33.8	9.2	52.3	0.04
57	300	35.6	4.4	60.0	0.06
58	350	22.6	1.1	76.0	0.06
59	350	31.8	2.4	65.9	0.05
60	400	12.5	1.3	86.3	0.04
61	400	28.5	1.3	70.0	0.04
62	450	23.1	3.1	72.3	0.05
63	450	18.5	3.1	76.9	0.05

Table 12.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Butylene	Ether	Alconol	Water
52	200	36.8	54.1	19.8	31.4
53	200	53.8	45.6	13.0	37.6
54	250	76.7	24.5	5.8	58.0
55	250	121.7	31.7	10.8	56.3
56	300	143.2	8.9	4.2	98.2
57	300	155.7	7.1	1.4	84.9
58	350	173.0	4.1	0.3	97.6
59	350	164.2	5.9	0.9	88.0
60	400	191.1	2.2	0.3	95.3
61	400	167.0	5.1	0.3	88.0
62	450	172.6	3.4	0.9	73.9
63	450	172.6	2.6	0.9	78.7

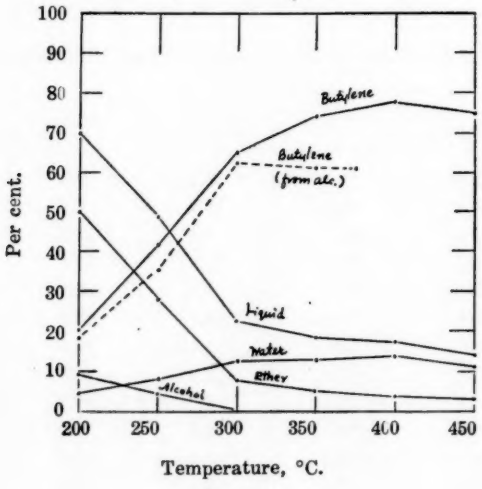

Fig. 6.

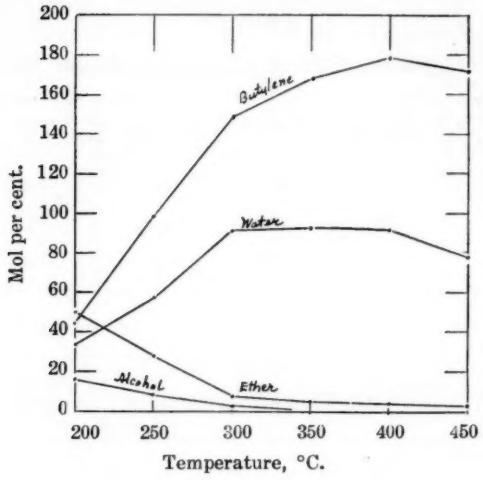

Fig. 7.

n-**Amyl Ether.** Pure ether of Eastman Kodak Co. is purified by distilling over metallic sodium, boiling point of which being 90–91°. The experimental conditions, decomposition products and the analytical results of the products are tabulated in Tables 13, 14, 15 and 16, and the mutual relations of the main products are shown in Figs. 8 and 9.

Table 13.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Amylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
64	45	250	0.3	41.0	0.3	45.3	91.1
65	45	300	0.3	42.0	0.4	67.1	93.3
66	45	350	0.3	42.0	0.4	74.8	93.3

Table 14.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
64	250	0	0.4	1.0	19.6	0	0
65	300	0	0.4	0	19.4	0	0
66	350	0	0	0	20.0	0	0

Table 15.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water	Aldehyde
64	250	49.7	35.4	8.1	6.8	+
65	300	71.9	17.1	2.7	8.8	+
66	350	80.1	8.1	0.8	11.0	+

Table 16.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water
64	250	102.2	32.2	13.3	54.7
65	300	162.4	15.9	4.5	68.4
66	350	180.8	7.6	1.4	89.8

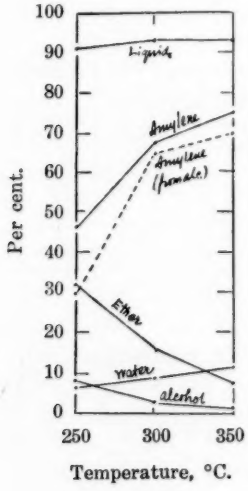

Fig. 8.

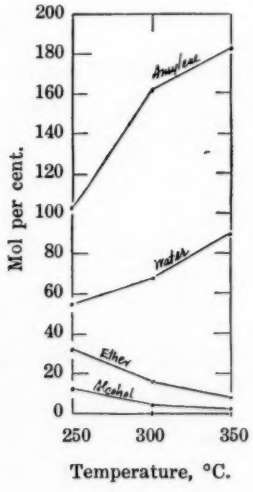

Fig. 9.

Ethyl-*n*-Butyl Ether. Pure product of Eastman Kodak Co. is repeatedly distilled over metallic sodium, boiling point of which being 91-91.5°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 17, 18, 19 and 20, and the mutual relations of the main products are shown in Figs. 10 and 11. The ether is also prepared from *n*-butyl alcohol and ethyl iodide using sodamide as a condensing agent, which is a good method for the preparation of the ether or of similar compounds.

Table 17.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %	Butylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.			
67	50	200	0.28	45	1.69	1.4	8.6	90.0
68	50	250	0.28	27	6.83	7.9	36.5	54.0
69	70	350	0.29	15	22.75	20.1	44.5	21.4

Table 18.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
67	200	75.4	0.4	1.0	5.0	4.2	6.2
68	250	90.2	3.0	0.4	2.2	2.0	1.2
69	350	90.2	3.2	0.6	1.4	2.4	2.2

Table 19.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Ethyl Alcohol	Butyl Alcohol	Water	Aldehyde	Low boiling fraction	High boiling fraction
67	200	46.6	7.7	1.7	6.0	+	26.9	11.1
68	250	24.2	9.6	1.1	19.3	+	35.0	9.8
69	350	9.1	1.1	trace	74.7	+	0.5	14.7

Table 20.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Ethylene	Butylene	Ether	Ethyl alcohol	Butyl alcohol	Water
67	200	5.0	15.6	41.9	15.5	2.1	30.6
68	250	28.6	66.5	13.1	11.5	0.8	59.0
69	350	73.3	80.4	2.0	4.4	trace	95.8

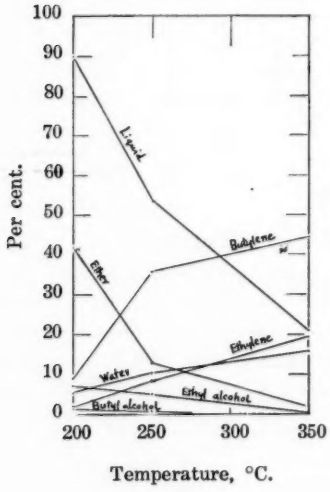

Fig. 10.

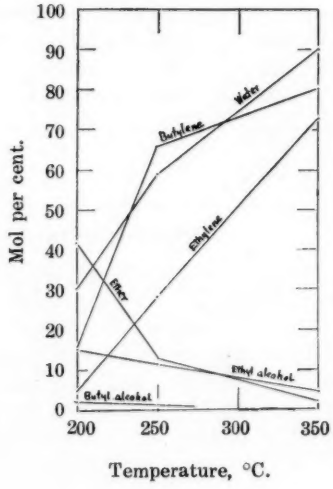

Fig. 11.

n-**Amyl Alcohol.** Pure product of Eastman Kodak Co. and of Kahlbaum is used after distilling over powdered quick lime, boiling point of which being 137-138°. The experimental conditions, decomposition products and analytical results of the products are summarised in Tables 21, 22, 23 and 24, and the mutual relations of the main products are shown in Fig. 12.

Table 21.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Amylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
70	45	250	0.3	43.0	0.23	29.5	95.6
71	45	300	0.3	42.5	0.44	64.9	94.4
72	45	350	0.3	42.5	0.36	70.0	94.4

Table 22.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
70	250	0	1.2	0.8	21.1	4.6	0
71	300	1.4	0.2	2.4	19.5	4.0	0
72	350	5	0.4	1.0	18.7	2.6	3.8

Table 23.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water	Aldehyde
70	250	30.8	6.2	53.2	9.8	+
71	300	68.7	4.5	3.1	19.1	+
72	350	74.1	4.0	1.2	20.5	+

Table 24.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water %
70	250	37.1	3.3	50.8	45.7
71	300	81.6	2.4	2.9	88.1
72	350	88.0	2.1	1.1	94.5

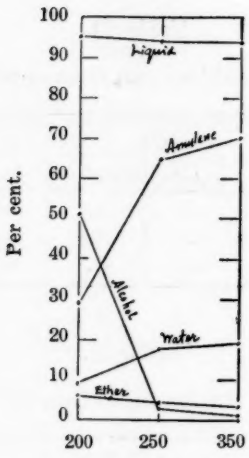

Fig. 12.

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November, 1929. Tokyo.